PB82-261371

Reactions of Chrome Tannery Sludge with Organic and Mineral Soils

(U.S.) Corvallis Environmental Research Lab., OR

21 Aug 81

U.S. Department of Commerce
National Technical Information Service
NTIS

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completi

1. REPORT NO.	2.	3. PB82-261371
EPA-600/J-82-216	JOURNAL ARTICLE	

4. TITLE AND SUBTITLE	5. REPORT DATE
Reactions of Chrome Tannery Sludge with Organic and Mineral Soils	1982
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
Carlos Wickliff, V.V. Volk, David T. Tingey, William L. Griffis, Marita Y. Trunk, Jack L. Witherow.	
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Environmental Research Laboratory Office of Research and Development U.S. Environmental Protection Agency Corvallis, Oregon 97333	11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
same	journal article - inhouse
	14. SPONSORING AGENCY CODE
	EPA/ORD/02

15. SUPPLEMENTARY NOTES

Published in Water, Air, and Soil Pollution 17 (1982) 61-74.

16. ABSTRACT

Chrome tannery sludge applied to agricultural land may have benefits in terms of added N for crop growth. An experiment was designed to compare tannery waste with commercial N fertilizer and investigate the potential of the waste as an alternative or supplement to commercial fertilizer. Soils with 38% and 7% organic C and N content of 1.3% and 0.2%, respectively, were amended with lime, commercial N fertilizer, or tannery sludge containing 1.6% Cr. A portion of the tannery waste was supplemented with additional Cr^{3+} salt before adding to the soils. The amended soils were analyzed for total Cr, ammonium acetate extractable Cr, selected nutrient and trace element concentrations. The tannery sludge increased soil pH, total Cr and N, S, Ca, P, Mg, and Na concentrations. DTPA extractable Cr increased only when Cr^{3+} salt was added, but soil pH decreased markedly. Electroconductivity exceeded values recommended for successful crop production. The acidic, high salt conditions complicated interpretation of the Cr^{3+} salt addition results. Tannery sludge may be applied to agricultural land as a fertilizer amendment without adversely affecting soil chemical properties. The amount and frequency of application should be determined by (1) total and available N, (2) total salt content, (3) total and available Cr, and (4) soil organic matter.

17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
Release to public	unclassified	
	20. SECURITY CLASS *(This page)*	22. PRICE
	unclassified	

EPA Form 2220-1 (9-73)

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA 22161

EPA-600/J-82-216
JOURNAL ARTICLE

REACTIONS OF CHROME TANNERY SLUDGE WITH ORGANIC AND MINERAL SOILS

CARLOS WICKLIFF,[1] V. V. VOLK,[2] DAVID T. TINGEY,[1] WILLIAM L. GRIFFIS,[1]
MARITA Y. TRUNK,[1] and JACK L. WITHEROW[3]
Terrestrial Division, Corvallis Environmental Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Corvallis, OR 97333, U.S.A.

(Received May 20, 1981; Revised August 21, 1981)

Abstract. Chrome tannery sludge applied to agricultural land may have benefits in terms of added N for crop growth. An experiment was designed to compare tannery waste with commercial N fertilizer and investigate the potential of the waste as an alternative or supplement to commercial fertilizer.

Soils with 38% and 7% organic C and N content of 1.3% and 0.2%, respectively, were amended with lime, commercial N fertilizer, or tannery sludge containing 1.6% Cr. A portion of the tannery waste was supplemented with additional Cr^{3+} salt before adding to the soils. The amended soils were analyzed for total Cr, ammonium acetate extractable Cr, selected nutrient and trace element concentrations.

The tannery sludge increased soil pH, total Cr and N, S, Ca, P, Mg, and Na concentrations. DTPA extractable Cr increased only when Cr^{3+} salt was added, but soil pH decreased markedly. Electroconductivity of the soils increased with the waste application rate and, at the highest rate of Cr^{3+} salt addition, far exceeded values recommended for successful crop production. The acidic, high salt conditions complicated interpretation of the Cr^{3+} salt addition results.

Tannery sludge may be applied to agricultural land as a fertilizer amendment without adversely affecting soil chemical properties. The amount and frequency of application should be determined by (1) total and available N, (2) total salt content, (3) total and available Cr, and (4) soil organic matter.

1. Introduction

Tanneries annually generate over 45 000 tonne of solid waste from Cr-mediated leather tanning operations (Conrad *et al.*, 1976). Approximately 60% of this waste is found in the wastewater from the hair removal and tanning operation.

Currently, tannery wastes are disposed of in landfills, trenches, or lagoons. Since the sludge contains elements such as Cr, Zn, Pb, Cu, Ni, and Cd, the disposal sites must be carefuly managed to eliminate percolation water and ensure control of trace element which may be hazardous to plants or human health.

Waste sludges from four tanneries varied considerably in their element content (Thorstensen and Shah, 1979). The dry sludges containes total N – 3 to 5%, NH_4–N – 0 to 0.6%, Ca – 1.2 to 12%, and Cr – <0.01 to 2%. The sludges also contained 5 to 39 mg Cr, 5 to 143 mg Zn, and 5 to 323 mg Pb per kg dry matter. Sludges from other

[1] U.S. Environmental Protection Agency, Corvallis Environmental Research Laboratory, Corvallis, Oregon 97333, U.S.A.
[2] Department of Soil Science, Oregon State University, Corvallis, Oregon 97331, U.S.A.
[3] U.S. Environmental Protection Agency, Robert S. Kerr Environmental Research Laboratory, Ada, Oklahoma 74820, U.S.A.

chrome tanneries contained 15.5 to 75.0 g Cr, 0.05 to 5.8 g Cu, <10–800 mg Pb kg^{-1} dry matter (Conrad *et al.*, 1976).

The application of tannery sludge to soil increases the amount of humic compounds and total N in the soil (Liska and Kozik, 1963). In one experiment reported by Liska and Kozik, total N increased 14 to 25% during 4 yr of sludge application; P, K, and Mg did not increase.

Tannery waste contains Cr salts which may reduce plant growth when their concentration is sufficiently high (Kick and Braun, 1977). When tannery sludge was added to loessial soil low in organic matter, a gleyed loam soil, and an acid sandy soil, the Cr concentrations in the soils increased from 80 to 2884 mg kg^{-1}. Spring rye, Serradella, green mustard, winter rye, winter wheat, spinach, and ryegrass growth decreased when the Cr concentration exceed 500 mg kg^{-1} and the pH was below 6.0. When lime was applied to the loessial and loam soils so that the pH exceed 6, crop growth decreased as Cr levels were raised to 1000 mg kg^{-1}. The Cr content of mustard, ryegrass, and spinach increased with Cr application to the soil. The Cr extracted from the soil by ammonium acetate increased with Cr application and was proportional to Cr uptake by the plants.

The following investigation was designed to determine the effects of tannery sludges on soil chemical properties.

2. Methods

2.1. Preparation of soil mixtures

Tannery sludge from the S. B. Foot Tanning Company, Redwing, Minnesota, was dried for 24 h in a forced draft oven at 50 C, pulverized in a hammermill, and sieved to pass a 2-mm screen. The dry sludge was characterized for lime equivalency, electroconductivity, and element content (Kauffman and Gardner, 1976).

Two acid soils, a Semiahmoo muck which contained approximately 38% organic C and an Amity silty clay loam soil (7% organic C), 0 to 20 cm depth, were collected from the Willamette Valley of western Oregon. The soils were air dried and sieved to pass a 2-mm screen.

Portions of the Amity and Semiahmoo soils were limed at the rates of 12.3 and 47.7 tonne ha^{-1} of calcium carbonate, respectively. The limed soils were allowed to equilibrate 6 weeks and then air dried. Samples of the soils were amended with tannery sludge at rates equivalent to one-half, one, and two times the normal agricultural application of available N for tall fescue, corn and bush bean crops. The available N in the sludge was calculated as the sum of the NH_4^+–N and NO_3^-–N extracted plus 18% of the organic N.

Prior to planting, additional samples of the acid and limed Amity soil were amended with commercial fertilizer, $(NH_4)_2SO_4$, at rates one-half, one, and two times the amount required for normal crop growth, according to soil tests and fertilizer guides (Extension Service, 1978). No commercial fertilizer was added to the Semiahmoo muck because it contained N in quantities equivalent to or greater than that required for normal crop growth.

Portions of the tannery sludge were mixed with sugar-reduced basic chromium sulfate (Cr^{3+}), the compound used in the chrome tanning operations. This compound was added to the tannery sludge so that the final Cr concentration was 10 and 100 times the initial Cr concentration of the sludge. These Cr-supplemented wastes were applied to the two soils using N as the guide element.

The soils were mixed thoroughly after adding of the tannery sludge and subsamples collected. Portions of each amended soil were placed in 1-gallon polyethylene pots and placed in the greenhouse. All treatments were replicated four times.

The sides and bottom of each pot were covered with opaque plastic to exclude light and prevent algal growth. This plastic was covered with aluminum foil during the summer months to reflect sunlight and reduce soil temperatures to ambient level in the greenhouse. Tall fescue (*Festuca arundinacia* L.) seeds (12), hybrid sweet corn (*Zea mays* L. cv. Jubilee) seeds (6), and bush bean (*Phaseolus vulgaris* L. cv. blue lake 53) seeds (6) were planted in the pots (Wickliff *et al.*, 1981). Soil water content was maintained at 50% field capacity by daily addition of reverse osmosed (R/O) water equal to that lost by evapotranspiration (Reuss *et al.*, 1978). The pots were weighed to determine water requirements. The greenhouse was maintained at 24 C during the day and 18 C at night.

The tall fescue was harvested on days 73, 146, and 292 after planting. The corn and bush beans were harvested on days 42 and 49, respectively. Soils in which the corn and bush bean plants were grown remained fallow for nine weeks after first harvest and then were replanted and harvested as before.

The soils used to grow tall fescue were sampled without disturbing the plants by using a small sampling tube to remove 100 g of soil from each container. Soils from 2 of the 4 replicates were combined into 200 g quantities to provide two samples for analysis per treatment.

2.2. Chemical analysis

The total element content of the tannery waste and soil was determined after digestion of subsamples with either nitric and hydrofluoric acids in a sealed plastic bottle (Wagner, 1977) or perchloric acid. Total K and Na in the waste was determined in the digestate solution by atomic absorption spectrophotometry. Total Mg, Ca, Fe, and the trace elements in the waste were determined in the same solution using the inductively coupled plasma emission spectrometer (McQuaker *et al.*, 1979). Total S content of the waste was determined in the solution by turbidometric sulfate determination (Am. Pub. Health Assoc., Am. Water Works Assoc. and Water Pollut. Control Fed., 1976).

To determine N content, each tannery sludge and soil sample was digested using a modified Kjeldahl procedure (Am. Pub. Health Assoc., Am. Water Works Assoc. and Water Pollut. Control Fed., 1976). In addition, NH_4^+–N and NO_3^-- plus NO_2^-–N were extracted from tannery sludge and soil with 2M KCl and phosphate-P was extracted with acid fluoride (Kauffman and Gardner, 1976). The total N and P content of these extractions was determined colorimetrically with a Technicon Autoanalyzer (Gales and Booth, 1974).

Soil pH was determined with a glass electrode pH meter when the electrode was placed in the supernatant formed after the soil settled from aqueous suspension (Kauffman and Gardner, 1976). The pH of the tannery waste was determined in the same manner. Soil electroconductivity was determined by measuring the electrical conductivity of a saturation extract of the soil (Kauffman and Gardner, 1976).

Ammonium acetate extractable Mg, K, Ca, and Na, and DTPA (diethylenetriamine pentaacetic acid) extractable trace elements (Kauffman and Gardner, 1976) in tannery sludge and soil were determined in solution using atomic absorption spectrophotometry.

Sulfate was extracted from soils with 1N KCl (Kauffman and Gardner, 1976) and determined in solution by turbidimetric sulfate determination (Am. Pub. Health Assoc., Am. Water Works Assoc. and Water Pollut. Control Fed., 1976).

The data were subjected to analysis of variance and least significant difference (LSD) values were computed.

3. Results and Discussion

3.1. Composition of Tannery Sludge

Tannery sludge contains most nutrients required by plants as well as several potentially hazardous trace elements, such as Cr, Zn, Cu, Ni, Pb, and B (Table I). The Cr (1.6%) and total N (2.9%) concentrations of the dry sludge used in these experiments were approximately half that which had been reported for other tannery wastes (Conrad *et al.*, 1976). Since the chemical composition of tannery sludge varies with source (Thorstensen and Shah, 1979), it is imperative that chemical analysis be completed before the sludge is applied to agricultural land.

TABLE I

Total and extractable constituents of tannery sludge

Constituent	Total	Constituent	Extractant
			2M KCl
N ($g\,kg^{-1}$)	29 ± 1		
Cr ($g\,kg^{-1}$)	16 ± 1	NH_4–N ($mg\,kg^{-1}$)	57 ± 7
P ($g\,kg^{-1}$)	1.4 ± 0.1	(NO_2 + NO_3)–N ($mg\,kg^{-1}$)	< 1.0
Ca ($g\,kg^{-1}$)	140 ± 10		
S ($g\,kg^{-1}$)	16 ± 1		Ammonium acetate
Mg ($g\,kg^{-1}$)	8 ± 5		
Na ($g\,kg^{-1}$)	6 ± 0.2	Mg ($mg\,kg^{-1}$)	327 ± 30
Fe ($g\,kg^{-1}$)	18 ± 0.4	K ($mg\,kg^{-1}$)	122 ± 4
Mn ($g\,kg^{-1}$)	1 ± 0.1	Na ($mg\,kg^{-1}$)	6050 ± 260
K ($g\,kg^{-1}$)	0.2 ± 0	Cl ($mg\,kg^{-1}$)	39 ± 1
Cu ($mg\,kg^{-1}$)	36 ± 3		
Ni ($mg\,kg^{-1}$)	36 ± 3		Acid fluoride
Zn ($mg\,kg^{-1}$)	182 ± 4	P ($mg\,kg^{-1}$)	1 ± 0
Pb ($mg\,kg^{-1}$)	128 ± 11		
B ($mg\,kg^{-1}$)	414 ± 20	pH	10.2 ± 0.1
Cd ($\mu g\,kg^{-1}$)	< 3.3		

3.2. Immediate effects of soil amendments

The initial pH of the Amity and Semiahmoo muck soils was identical before the sludge and fertilizer amendments (Tables II and III). The mean concentration of organic C in the Semiahmoo muck (228 g kg^{-1}), however, was more than three times that of the Amity soil (71 g kg^{-1}). The NH_4–N and NO_3^-- plus NO_2^-–N content of the Semiahmoo soil was consistently greater than that of the Amity soil. Of all the ammonium acetate and DTPA extractable elements assayed, only Mn had a greater concentration in the Amity soil than in the Semiahmoo soil.

Immediately after application of the tannery sludge, the soil pH increased (Table II); however, the immediate pH increase was less than that which occurred after lime application. Because of the greater buffer capacity, the pH of the Semiahmoo soil did not increase as much as that of the Amity soil with an equal application of the waste.

The electroconductivity of both soils increased with tannery sludge, N fertilizer, and lime additions (Table II). Lime plus tannery sludge or N fertilizer increased the electroconductivity of both soils markedly. The inorganic C content of the soil-sludge mixtures increased, probably reflecting the carbonate in the waste. The inorganic C content of each soil was still low even after application of the sludge waste.

The amount of N added as fertilizer was small compared to total N in the Amity soil so no changes in total N were observed nor would they be expected (Table II). The NH_4–N content of the Amity soil did increase with the fertilizer application. A slight increase in total N was observed in both soils when tannery waste was applied since a larger quantity of total N was added. Sulfate-S increased in both soils as a function of waste and supplemental Cr salt application. Since the Cr was applied as a sulfate salt, increases in SO_4–S content were to be expected. The ammonium acetate extractable Ca increased with waste and lime application and extractable Na increased in both soils upon application of the tannery waste. The NO_3^-- plus NO_2^-–N and DTPA extractable Cu did not change with the application of the tannery waste to the Amity soil.

DTPA extractable Cu decreased only in the Semiahmoo soil to which lime was added, but DTPA extractable Mn and acid fluoride extractable P decreased in both soils when either lime or tannery sludge, or both were added. The decreases occurred most likely because of the soil pH increase and reduced solubility of Cu, P, and Mn compounds (Brady, 1974; Lindsay, 1979). The Mn contents of lime-amended Semiahmoo muck soils were very low and could be considered deficient for normal plant growth (Brady, 1974).

DTPA extractable Zn decreased in the Amity soil while Pb decreased in both soils when carbonate was added (Table III). DTPA extractable Ni and Cd decreased only in the Semiahmoo soil to which both tannery waste and carbonate had been added. However, Cd increased in the Semiahmoo soil with tannery waste application without additional carbonate.

3.3. Effects on tall fescue crop

Dry matter yields of the first tall fescue crop increased when tannery waste was added to both soils although to a smaller extent than with commerical N (Wickliff *et al.*, 1981).

TABLE II

Chemical analysis of soils prior to cropping

Tannery sludge tonne ha^{-1}	Commercial fertilizer kg–N ha^{-1}	$CaCO_3$ tonne ha^{-1}	pH	EC mmho cm^{-1}	Total inorg. C g kg^{-1}	Total N g kg^{-1}	2M KCl Extractable		IN KCl Extractable SO_4–S mg kg^{-1}	Acid F$^-$ Extractable P mg kg^{-1}
							NH_4–N mg kg^{-1}	[a]$(NO_2 + NO_3)$–N mg kg^{-1}		
			Amity silty clay loam							
	0		5.5	0.1	0.04	1.8	4	<1.0[b]	0.7	27
	90		[c]	0.5	[c]	1.7	5	1.2	[c]	16
	180		[c]	0.9	[c]	1.8	78	1.1	[c]	14
	360		[c]	1.3	[c]	2.2	175	2.2	[c]	34
10.6			5.9	[c]	0.24	2.2	3	<0.4[b]	9.7	11
21.2			6.2	1.5	0.49	2.4	3	<0.3[c]	18.5	10
42.4			6.9	3.0	1.18	2.6	4	0.4	36.0	9
	0	12.3	6.7	0.3	0.11	1.5	4	3.7	1.2	11
	360	12.3	6.8	1.2	[c]	[c]	[c]	[c]	[c]	15
42.4		12.3	7.3	2.8	1.16	2.1	10	0.4[b]	31.0	6
			Semiahmoo muck							
0			5.5	1.0	0.04	13.1	7	46	3.6	[c]
10.6			6.1	2.1	0.29	15.3	6	47	24.7	86
21.2			6.2	3.0	0.55	15.8	8	29	26.5	70
42.4			6.6	4.0	1.16	15.9	5	25	37.0	59
		47.7	7.2	1.6	1.33	11.6	8	66	7.0	50
42.4		47.7	7.1	2.9	2.78	11.2	37	9	51.7	30
		LSD (5%)	0.22	0.2	0.08	0.5	30	3.0	0.9	5.0

[a] Data from soils cropped to corn; data from soils cropped to tall fescue unavailable.
[b] Sample size insufficient for accurate analysis.
[c] Not analyzed.

TABLE III

Extractable element content of soils prior to cropping

Tannery sludge tonne ha^{-1}	Commercial fertilizer kg–N ha^{-1}	$CaCO_3$ tonne ha^{-1}	NH_4OAc			DTPA						
			K g kg^{-1}	K mg kg^{-1}	Na mg kg^{-1}	Fe mg kg^{-1}	Pb mg kg^{-1}	Cu mg kg^{-1}	Zn mg kg^{-1}	Mn mg kg^{-1}	Ni mg kg^{-1}	Cd mg kg^{-1}
			Amity silty clay loam									
	0		1.5	160	34	199	0.3	1.4	1.8	50	0.6	<0.04[a]
	90		[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]
	180		[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]
	360		[b]	[b]	3	[b]	[b]	[b]	[b]	[b]	[b]	[b]
10.6			2.3	213	83	138	1.0	1.5	1.5	33	1.0	<0.04[a]
21.2			2.9	159	110	124	0.7	1.5	1.6	31	<0.8[a]	<0.04[a]
42.4			3.4	154	162	125	0.7	1.7	2.1	35	<0.8[a]	<0.04[a]
	0	12.3	3.7	186	44	111	0.4	1.3	0.7	9	<0.8[a]	<0.06[a]
	360	12.3	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]
42.4		12.3	3.3	192	161	77	0.5	1.4	1.5	19	<0.8[a]	<0.04[a]
			Semiahmoo muck									
0			[b]	486	56	188	0.1	4.2	10.0	17	1.5	<0.04[a]
10.6			3.6	565	121	340	0.7	4.2	12.0	11	1.1	0.46
21.2			3.7	580	141	380	0.6	5.2	12.0	10	1.4	0.58
42.4			3.7	340	210	352	0.8	3.8	12.0	2	1.2	0.61
		47.7	3.2	435	73	190	0.3	2.1	10.0	9	1.2	0.42
42.4		47.7	3.7	409	197	123	0.3	1.1	7.0	1	0.8	0.26
		LSD (5%)	0.3	70	5	7	0.2	1.2	0.2	4	0.2	0.16

[a] Sample size insufficient for accurate analysis.
[b] Not analyzed.

Yields at subsequent croppings increased to a greater extent with the tannery waste than with the commercial N.

Plants grew less than 6% of the dry weight of the control or not at all in soils amended with tannery sludge that contained the highest level of total Cr (Wickliff *et al.*, 1981). The Cr concentration in the tops of plants grown in soil with the highest Cr level was 3 times that in the tops of plants grown on non-amended soil.

3.4. Soil chemical changes after tall fescue cropping

After cropping the soils with tall fescue the electroconductivity of both soils increased at the two highest waste applications and with the application of the Cr salts (Table IV). The EC of the Amity soil which received the highest Cr application far exceeded values recommended for successful agricultural production.

After cropping, the pH of the Amity soil decreased with application of the NH_4–N fertilizer (Table IV). This decrease would be expected as a function of the oxidation of NH_4^+ to NO_3^- with the release of hydronium ions (Brady, 1974). The pH of those soils which had received the extra Cr was much lower than for any other soil treatments. Along with the high EC, the low pH of the Cr-treated soils caused problems in the interpretation of Cr toxicity versus other trace element toxicities which may occur under acidic conditions.

No difference in the final values of total N and inorganic C were observed as a function of waste or fertilizer application (Table IV). The NH_4–N concentration of those soils which were treated with the highest rate of Cr was larger than for all other waste, N, or calcium carbonate applications. It may be possible that the nitrification of NH_4–N present in the system was inhibited by the acidic, high salt conditions more than by the high Cr content. Nitrification in a sandy loam soil was inhibited completely when the EC was 47.8 mmho cm^{-1} at neutral pH reaction (Laura, 1977). Nitrification is sharply curtailed at pH values below 5.5 (Brady, 1974).

Nickel extracted by DTPA increased only when the highest rate of Cr salt was added in the Amity soil (Table V). This increase most likely related to the more acidic conditions present after application of the Cr salt. No change in DTPA extractable Ni was observed in the Semiahmoo soil, probably because the Ni complex formed with the organic materials was stronger than could be extracted by DTPA (Stevenson, 1976).

KCl extractable NO_2^-- plus NO_3^-–N increased in the Amity soil, but decreased in the Semiahmoo soil after cropping regardless of whether commercial fertilizer or waste materials were applied (Table IV). Plants grew larger in the Semiahmoo than in the Amity soil (Wickliff *et al.*, 1981) and probably depleted the NO_3–N since NH_4–N also decreased and therefore did not provide substrate for nitrification. Leaching of nitrate is not a probable cause of the decreased NO_3–N levels because leaching was prevented by the closed pots. The $NO_{2-}^- + NO_3^-$–N in the Semiahmoo soil to which line and the largest amount of Cr had been added was higher than in any of the other treatments. Interpretation of these results is complicated by the high salt conditions that accompanied Cr salt addition.

After cropping, the acid fluoride extractable P in the Amity soil decreased with waste

TABLE IV

Chemical analysis of soils after cropping with tall fescue

Tannery sludge tonne ha^{-1}	Commercial fertilizer kg–N ha^{-1}	$CaCO_3$ tonne ha^{-1}	Added Cr g kg^{-1}	pH	EC mmho cm^{-1}	Total inorg. C g kg^{-1}	Total N g kg^{-1}	2M KCl Extractable		IN KCl Extractable SO_4–S mg kg^{-1}	Acid F^- Extractable P mg kg^{-1}
								NH_4–N mg kg^{-1}	[a] $(NO_2 + NO_3)$–N mg kg^{-1}		
				Amity silty clay loam							
	0			5.6	1.5	0.03	2	2	8	5	21
	90			5.5	0.2	0.06	2	<2[b]	<4[b]	62	13
	180			5.3	0.3	0.05	2	<2[b]	27	14	9
	360			5.2	0.5	0.08	2	2	39	12	16
10.6				5.7	0.6	0.05	2	2	<4[b]	17	<6[b]
21.2				6.2	1.3	0.07	2	2	32	47	<4[b]
42.4				6.9	1.9	0.07	2	3	150	99	<4[b]
21.2			1.37	5.0	8.8	0.06	2	5	6	2100	<4[b]
21.2			15.1	3.8	73.0	0.06	2	9	<4[b]	7500	5
	0	12.3		7.0	0.3	0.08	2	2	14	24	<4[b]
	360	12.3		6.7	1.1	0.07	2	2	160	107	12
42.4		12.3		7.5	1.8	[c]	2	3	225	79	<4[b]
42.4		12.3	14.9	3.6	20.3	0.05	2	3	<4[b]	4333	<4[b]
				Semiahoo muck							
0				6.3	0.6	[c]	13	5	5	7	78
10.6				5.8	0.6	0.07	14	4	12	26	115
21.2				6.1	0.6	0.06	14	4	17	21	86
42.4				6.6	0.8	0.09	14	4	9	29	33
21.2			1.34	5.6	7.3	0.07	14	4	9	1184	60
21.2			14.8	4.9	43.0	0.06	11	34	7	5000	<7[b]
		47.7		6.7	0.5	[c]	12	5	10	<7[b]	83
42.4		47.7		7.5	1.3	[c]	13	4	40	<60[b]	15
42.4		47.7	14	6.5	27.9	0.10	11	4	105	2700	<4[b]
		LSD (5%)		0.8	1.0	0.02	1	1	31	6	3

[a]Data from soils cropped to corn; data from soils cropped to fall fescue was not unavailable.
[b] Sample size insufficient for accurate analysis.
[c]Not analyzed.

and lime application. Phosphorus is most available as a plant nutrient at mineral soil pH 6–7 (Brady, 1974). The pH of the Amity soil was 6.7 to 7.5, and depended on the quantity of waste applied. The decrease in extractable P indicates decreased availability of P as a result of carbonate addition to the soil, irregardless of whether it is added as lime alone or in tannery waste. No consistent change in K concentration could be observed in the soil as a function of fertilizer, waste, or lime application (Table V). The application of the Cr salt did increase the amount of K extracted from both the Amity and Semiahmoo soils. This increase most likely related to the very acidic conditions which were present after application of the Cr salt.

The extractable Na content of the Amity soil did not change upon application of the commercial fertilizer material but did increase with the tannery waste application (Table V). This would be expected because of Na present in the tannery waste. An exceptionally large increase in the Na concentration was observed after application of the Cr salt treatment to both soils. This was surprising because Na was not a constituent in the sugar-reduced basic chromium sulfate added to the Cr-treated soils (Hamblet and Hayes Co., 1977).

The Fe extracted by DTPA decreased with application of tannery waste and lime to the Amity soil (Table V). The application of lime decreased the Fe extracted from the Semiahmoo muck soil. The Pb, Cu, and Zn extracted from both soils after crop growth did not change as a function of fertilizer or waste application.

The DTPA extractable Mn was greater for the Amity soil after cropping than for the Semiahmoo muck soil (Table V). Presumably, this greater extraction of Mn relates to the formation of Mn organic chelates in the muck soil which could not be extracted by the DTPA (Brady, 1974). An increase in Mn extracted by DTPA was observed upon application of the commercial fertilizer product to Amity soil. However, upon application of the waste and liming materials the amount of Mn which could be extracted from the Amity soil was reduced.

3.5. Chromium effects

The application of Cr salt decreased the amount of Fe which was extracted from both soils (Table V). Surprisingly, the decrease occurred despite a pH decrease with the Cr salt application. The Cr treatment decreased the Cu and Zn extracted from both soils similar to that which was observed for Fe.

The DTPA extractable Pb content decreased only at the highest Cr application to the Amity soil despite the reduction in soil pH (Table V). DTPA extractable Cd decreased only in the Semiahmoo soil at the highest Cr application, despite the reduction in soil pH. The decrease in Cd also occurred when lime was added with the Cr.

Application of the Cr salt appeared to increase the amount of Mn extracted from both soils when lime was not applied.

Total Cr, as expected, increased in the soil-sludge mixtures with application of the tannery waste or Cr salt (Table VI). Total Cr measured at the end of the experiment was not different from that at the beginning.

DTPA extractable Cr could be accurately measured in the Amity soil only after Cr

TABLE V

Final extractable elemental content of soils after cropping with tall fescue

Tannery sludge tonne ha^{-1}	Commercial fertilizer kg–N ha^{-1}	$CaCO_3$ tonne ha^{-1}	Added Cr g kg^{-1}	NH_4OAc			DTPA						
				Ca g kg^{-1}	K mg kg^{-1}	Na mg kg^{-1}	Fe mg kg^{-1}	Pb mg kg^{-1}	Cu mg kg^{-1}	Zn mg kg^{-1}	Mn mg kg^{-1}	Ni mg kg^{-1}	Cd mg kg^{-1}
				Amity silty clay loam									
	0			1.5	145	47	195	4.0	1.6	1.7	56	0.7	0.1
	90			1.5	155	42	144	2.0	1.6	2.1	54	0.7	0.1
	180			1.5	145	42	166	2.2	1.6	2.6	49	0.7	0.1
	360			1.3	174	47	174	1.9	1.6	3.4	58	0.6	0.1
10.6				2.0	134	79	139	2.4	1.8	2.0	38	0.4	0.1
21.2				2.8	110	95	96	3.0	1.4	1.2	17	0.6	0.1
42.4				3.9	92	128	65	2.3	1.4	1.6	13	<0.3[a]	<0.1[a]
21.2			1.37	2.9	127	870	83	1.0	1.2	1.5	155	0.5	<0.1[a]
21.2			15.1	2.6	195	9700	117	1.5	0.3	1.0	280	1.7	<0.1[a]
	0	12.3		3.2	122	35	70	3.0	1.4	3.8	12	0.2	0.1
	360	12.3		3.2	132	35	91	2.1	1.5	1.8	22	0.3	0.1
42.4		12.3		5.8	98	138	84	1.9	1.9	3.2	29	0.5	0.1
42.4		12.3	14.9	5.7	195	8600	48	0.1	<0.5[a]	0.6	26	0.9	<0.1[a]
				Semiahmoo muck									
0				9.6	255	66	390	1.2	4.2	9.8	6	1.8	0.6
10.6				9.6	240	99	550	1.8	3.1	12.4	6	1.5	0.5
21.2				10.4	193	106	400	1.9	3.3	12.6	6	2.3	0.5
42.4				11.5	161	123	420	2.5	3.3	12.7	6	1.8	0.6
21.2			1.34	9.9	330	1 350	360	0.4	3.0	10.5	11	1.7	0.5
21.2			14.8	11.5	520	11 750	115	0.5	1.0	10.7	60	2.0	0.2
		47.7		12.0	250	63	360	0.7	3.2	10.6	7	1.8	0.6
42.4		47.7		14.0	124	132	310	0.4	2.8	10.0	15	1.7	0.4
42.4		47.7	14.6	16.5	320	12 000	141	0.7	1.6	4.8	10	1.9	0.2
		LSD (5%)		1.7	7	296	56	0.7	0.2	0.2	3	0.4	0.1

[a] Sample size insufficient for accurate analysis.

TABLE VI

Chromium concentrations in soils treated with tannery waste

Tannery sludge tonne ha^{-1}	Commercial fertilizer kg–N ha^{-1}	$CaCO_3$ tonne ha^{-1}	Added Cr g kg^{-1}	Total Cr		DTPA Extractable Cr	
				Immediate g kg^{-1}	After cropping g kg^{-1}	Immediate mg kg^{-1}	After cropping mg kg^{-1}
				Amity silty clay loam			
	0			0.07	0.03	<0.1[a]	<0.1[a]
	90			[b]	0.05	[b]	<0.2[a]
	180			[b]	0.03	[b]	<0.2[a]
	360			[b]	0.05	[b]	<0.2[a]
10.6				0.17	0.14	<0.1[a]	<0.2[a]
21.2				0.27	0.21	<0.1[a]	<0.2[a]
42.4				0.45	0.46	[b]	0.2
21.2			1.37	1.6	2.00	1.0	0.6
21.2			15.1	20.0	14.00	2050.0	2400.0
	0	12.3		[b]	0.03	[b]	0.3
	360	12.3		[b]	0.03	[b]	<0.2[a]
42.4		12.3		0.46	0.35	0.1	<0.2[a]
42.4		12.3	14.9	25.0	15.00	44.5	6.9
				Semiahmoo muck			
0				0.12	0.08	<0.1[a]	<0.2[a]
10.6				0.26	0.20	<0.1[a]	<0.2[a]
21.2				0.46	0.35	<0.1[a]	<0.2[a]
42.4				0.68	0.55	<0.1[a]	<0.2[a]
21.2			1.34	2.9	2.20	1.0	0.9
21.2			14.8	21.0	18.50	16.0	1.6
		47.7		0.08	0.09	[b]	<0.2[a]
42.4		47.7		0.43	0.49	<0.1[a]	<0.2[a]
42.4		47.7	14.6	20.0	19.00	1.6	0.7
		LSD (5%)		2.81	0.04	24.9	28.8

[a] Sample size insufficient for accurate analysis.
[b] Not analyzed.

salt or lime was added (Table VI). In the Semiahmoo soil, extractable Cr was measurable only when the Cr salt was added. In a prior experiment, the Cr content of topsoil increased markedly with tannery waste application (Liska and Kozik, 1963); however, the Cr accumulated in forms largely insoluble in aqueous solution. Only 1 to 4% of the total Cr was extracted in 2.5% acetic acid.

DTPA extractable Cr increased with, but not in proportion to, the amount of Cr salt added to both soils (Table VI). The detectable DTPA extractable Cr increased only when the Cr salt was applied. The observed increase was consistently greater for the Amity soil than for the Semiahmoo muck. This observed increase probably relates to chelation of applied Cr by the organic constituents of the Semiahmoo muck (Stevenson, 1976). These chelated Cr compounds were not extracted by DTPA. Liming both soils decreased the amount of extractable Cr.

3.6. Soils cropped to bush bean and corn

The results of experiments with the Amity and Semiahmoo soils cropped to bush bean and corn were similar to those discussed above. Although the soils growing bush bean and corn were disturbed between samplings the trends in chemical properties and element content were nearly identical to those observed in soils planted with tall fescue, which was not disturbed. This supports the previously discussed results of the experiment with tall fescue.

4. Conclusions

Tannery sludge supplies both plant nutrients (N, Ca, and S) and potentially toxic elements (Cr and Pb) to soils. Although in this experiment, the Cr was added to soils in a slightly soluble form, it was added in quantities several times the typical concentration in soil. Total Cr increased in proportion to Cr addition. Soil EC increased markedly with tannery sludge, but DTPA extractable Cr did not. Ammonium acetate extractable Na increased markedly in soils with tannery waste addition. The high salt content of the sludge may increase the salt content in soils sufficiently to reduce plant establishment. Therefore, crop yields may be decreased by excessive salt content in the soil before the Cr concentration becomes high enough to adversely affect yields. However, the results of prior research indicate that Cr, in concentrations in excess of 500 mg kg^{-1} of soil, can decrease yields of some crops when soil pH is below 6.0. The Semiahmoo muck contained 3.2 times as much organic C as the Amity soil, but the detectable DTPA extractable Cr was consistently lower in the Semiahmoo. A soil with a high concentration of organic constituents will reduce the amount of Cr available to plants.

Tannery sludges may be applied to agricultural soils as N fertilizer without adversely affecting soil chemical properties; but, they should not be applied indiscriminately since pH and salt content increase and the extractable concentration of Mn is decreased. The amount and frequency of tannery waste addition to soils should be determined by: (1) total N, (2) available N, (3) total salt content, (4) total and extractable Cr, and (5) soil organic matter.

Acknowledgments

The authors gratefully acknowledge the technical assistance of Joanne C. Oshiro and Amy M. Van Leer in the maintenance of soils and collection of samples, and of Claudia J. Wise in the analysis of soil samples.

References

Am. Pub. Health Assoc., Am. Water Works Assoc. and Water Pollut. Control Fed.: 1976, *Standard Methods for the Examination of Water and Wastewater*. Mary A. Franson (ed.). 14th ed. American Public Health Assoc., Washington, D.C.

Brady, N.C.: 1974, *The Nature and Properties of Soils*, MacMillan Publishing Co., Inc., New York.

Conrad, E. T., Mitchell, G. S., and Bauer, D. H.: 1976, *U.S. EPA Assessment of Industrial Hazardous Waste Practices – Leather Tanning and Finishing Industry*. A. Pearce (ed.). Hazardous Waste Management Division, Office of Solid Waste, USEPA, Washington, D.C.

Extension Service: 1978, Oregon State University, Corvallis.

Gales, M. E., Jr. and Booth, R. L.: 1974, *Simultaneous and Automated Determination of Total Phosphorus and Total Kjeldahl Nitrogen*, USEPA, Cincinnati, Ohio.

Hamblet and Hayes Co.: 1977, Personal Communication, Salem, Massachusetts.

Kauffman, M. D. and Gardner, E. H.: 1976, *Methods of Soil Analysis Used in the Soil Testing Laboratory at Oregon State University*. Special Report 321. Agr. Expt. Sta., Oregon State University, Corvallis.

Kick, V. H. and Braun, B.: 1977, *Landwirtsch. Forsch.* **30** (2): 160 (Ger.).

Laura, R. D.: 1977, *Soil Biol. Biochem.* **9**, 333.

Lindsay, W. L.: 1979, *Chemical Equilibria in Soils*, John Wiley and Sons, New York.

Liska, J. and Kozik, J.: 1963, *Za Vysoku Uroda* **9**, 347 (Pol.).

McQuaker, N. R., Kluckner, P. D., and Chang, G. N.: 1979, *Anal. Chem.* **51**, 888.

Reuss, J. O., Dooley, H. L., and Griffis, W.: 1978, *J. Environ. Qual.* **7**, 128.

Stevenson, F. J.: 1976, in J. O. Nriagu (ed.), *Environmental Biogeochemistry*, Vol. 2. Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan.

Thorstensen, T. C. and Shah, M.: 1979, *J. Am. Leather Chem. Assoc.* **74**, 14.

Wagner, J.: 1977, Personal communication, USEPA, Environmental Research Laboratory, Corvallis, Oregon.

Wickliff, C., Volk, V. V., Tingey, D. T., Griffis, W. L., Trunk, M. Y., and Witherow, J. L.: 1981 (in preparation).